

ADDITIONAL CLARIFICATION OF HYPOTHESES

***** DRAFT *****

During the September 22 workgroup meeting, there was continued discussion over the various hypotheses and some confusion over what some of them mean. The attached draft write-up is another step towards further refinement. We hope to spend some time at our November 16, 1999 workgroup meeting discussing this.

Revised “Hypotheses” [LCL – 11/09/1999]

The following hypotheses are discussed in this document:

1. NO_x reduction hypothesis
2. NO_x timing hypothesis
3. “Carryover” hypotheses
4. Weekend emission increase hypothesis

These hypotheses are not necessarily mutually exclusive, as two, three, or possibly even all four may be needed to explain the weekend effect in all locations. As the research progresses, other hypotheses may be proposed. Rather than define tasks according to address these specific hypotheses, the analyses being conducted pursue fundamental information that can be assembled flexibly to address many alternative and complex hypotheses.

These hypotheses represent alternative cause-and-effect explanations for observed differences in the concentrations of ozone and ozone precursors by day of week in the South Coast Air Basin. Ambient data indicate that NO_x and VOC's in the South Coast decrease on Saturday compared to Friday and on Sunday compared to Saturday while ozone concentrations at most sites increase. Each hypothesis is offered as a scientific proposition. The available data will be compared to the hypotheses to see which hypotheses provide a consistent explanation of the data.

The central premise of the NO_x reduction hypothesis is that transitions from Friday to Saturday and from Saturday to Sunday *provide an empirical laboratory* in which to observe the likely effects of a general NO_x reduction strategy. If this premise were correct, then we would expect a VOC reduction strategy in the South Coast to reduce ozone, whereas simultaneous NO_x reductions will erode the benefits of the VOC reductions. Furthermore, in the absence of VOC reductions, we would expect NO_x reductions to increase ozone concentrations.

The central premise of hypotheses 2, 3, and 4, is that transitions from Friday to Saturday and from Saturday to Sunday *do not provide an empirical laboratory* in which to observe the likely effects of a general NO_x reduction strategy. According to these hypotheses, emissions on weekend days differ in important respects; these differences strongly affect ozone production apart from any overall NO_x reductions. If one or more of these three hypotheses is correct, then a combined strategy of VOC and NO_x reductions may be most effective in maintaining the rapid rate of progress achieved in recent years in the South Coast.

1. NO_x Reduction Hypothesis

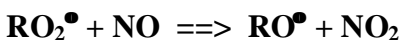
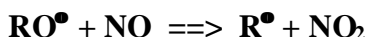
A. Theory

This hypothesis was formerly known as the “NO_x-disbenefit hypothesis”. According to this hypothesis, the overall VOC/NO_x ratio is the dominant factor influencing daily ozone concentration. The basin currently is characterized by a low VOC/NO_x ratio, indicating that the basin is primarily “hydrocarbon limited” or “hydrocarbon sensitive.” On weekends, NO_x is reduced substantially more than VOC’s leading to a significantly higher VOC/NO_x ratio and the higher VOC/NO_x ratio leads to higher ozone concentrations.

The photochemical production of ozone from VOC’s and NO_x has been studied extensively. It is well known that ozone producing systems are nonlinear, that is that a change in the amount of ozone produced is not directly proportional to the changes in precursor concentrations. Simple EKMA diagrams, such as the schematic example in Figure 1, illustrate the nonlinear relationships and indicate two general sets of conditions. When VOC/NO_x ratios are low, we expect benefits from VOC reductions and disbenefits from NO_x reductions. However, when VOC/NO_x ratios are high, we expect benefits from NO_x reductions and a neutral response to VOC reductions.

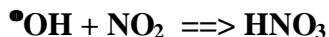
The basic reason for the shape of the ozone isopleths in an EKMA diagram is that NO_x participates in reactions that compete with one another. NO_x participates in radical propagation reactions that enhance ozone formation and in radical termination or “quenching” reactions that retard ozone formation. The VOC/NO_x ratio helps determine whether NO_x behaves as a net ozone generator (benefits result from NO_x reductions) or a net ozone inhibitor (disbenefits result from NO_x reductions).

**Example Reactions in which radicals recycle NO to NO₂
so the NO₂ can undergo photolysis and generate ozone
(Prominent in chemistry when reducing NO_x reduces ozone)**



(R is an organic molecule)

**Example reaction in which a hydroxyl radical is terminated by NO₂
removing both the radical and the NO₂ from the ozone generating system
(Prominent in chemistry when reducing NO_x increases ozone)**



B. Related Evidence

The available ambient air quality data indicate (at least tentatively) the following:

- total NO_x and HC emissions are reduced from Friday to Saturday
- total NO_x and HC emissions are reduced again from Saturday to Sunday
- NO_x is reduced substantially more (proportionally) than HC's.
- At most South Coast sites, weekend ozone levels are higher than the weekday levels, with Saturday higher than Friday and Sunday higher than Saturday

2. NO_x Timing Hypothesis

A. Theory

This hypothesis was formerly known as the “NO_x-limitation hypothesis”. According to this hypothesis, a dramatic difference in the timing of NO_x emissions is the primary cause of higher weekend ozone. If, in fact, the timing of NO_x emissions on weekend days is radically different from the timing on weekdays, the ozone production from mid-day NO_x emissions may be greatly increased. According to this hypothesis, higher weekend ozone concentrations may result from lower NO_x emissions primarily because of the timing of these emissions. Conversely, if NO_x emissions were proportionally lower for all hours of the day, as would likely occur under a general NO_x reduction strategy, this hypothesis suggests that weekends would not experience ozone increases relative to weekdays.

Hypothetically, low NO_x in the hours between sunrise and 10:00 to 11:00 a.m. allows the generation of radicals and ozone without NO_x “quenching”. By mid-day on weekends, the photochemistry becomes NO_x limited whereas weekday photochemistry still has an excess of NO_x during the mid-day hours. When weekend NO_x emissions increase during the mid-day hours, they would quickly convert to NO₂ and undergo photolysis leading to higher ozone. This general phenomenon is well-known in smog chamber studies (see Figure 2).

B. Related Evidence

The available data indicate (at least tentatively) the following in addition to the points noted under the previous hypothesis:

- traffic data indicate much less activity on weekend mornings but only slightly less activity in the mid-day hours compared to weekdays
- air quality data indicate that weekend NO_x emissions from 6 a.m. to 10 a.m. are much lower compared to weekdays, perhaps 30% to 60% lower. From 11 a.m. to 2 p.m., however, NO_x emissions may approach (in some locations may surpass?) the rate of weekday emissions
- in the 1990's, ozone decreased substantially on all days of the week, but weekday ozone decreased faster than weekend ozone – estimated decreases based on May to October data for 1989-1991 (baseline) and 1996-1998 are 31% mid-week (Tue - Thu), 24% on Saturdays, and 21% on Sundays
- throughout the 1990's, reductions in NO_x and HC from weekdays to weekends were similar, with overall weekend decreases of approximately 20% HC and 40% NO_x in 1990's for the hours between 6 a.m. and 12 noon
- emission inventories indicate that VOC emissions decreased faster than NO_x from 1990 to 1995 — a 20% decrease for VOC and a 12% decrease for NO_x
- During the course of a day, the photochemistry tends to become NO_x-sensitive because NO_x is removed much faster than VOC from the atmospheric system (Lu and Chang, 1998)
- even if VOC/NO_x ratios remain constant, as emissions decrease photochemistry seems to shift toward more NO_x-sensitive conditions (Lu and Chang, 1998)

3. “Carryover” Hypotheses

Two hypotheses are proposed under the “carryover” banner.

Carryover hypothesis #1

A. Theory

This hypothesis states that the higher weekend ozone concentrations occur because extra emissions from traffic on Friday and Saturday nights are injected into the nocturnal boundary layer. These extra emissions then lead to greater ozone formation after sunrise on the following day.

B. Related Evidence

Traffic count data lend some support to this idea. In addition, ambient air quality data at some sites (e.g., downtown L.A.) show NO_x concentrations from 6 p.m. to midnight to be substantially higher compared to other days of the week. However, air quality data also show substantially lower NO_x and HC levels on Saturday and Sunday mornings from 6 a.m. to Noon rather than the increased levels postulated under this hypothesis.

- traffic in the evening hours (perhaps, from 6 p.m. to 2 a.m.) appears to be greater on Friday and Saturday at many sites compared to other days of the week. However, the number of vehicles during these hours is relatively small compared to the number of vehicles during weekday commute hours
- presumably, emissions from the extra evening traffic become trapped near the surface as the ground-based inversion layer develops on most days
- several studies, however, have found lower concentrations of NO_x and HC at the surface on Saturday and Sunday in the morning hours from 6 a.m. to Noon compared to weekdays
- traffic data indicate higher than normal vehicle counts on Friday and Saturday evenings from 9 p.m. to 4 a.m.

Carryover hypothesis #2

A. Theory

This hypothesis states that pollutants (primarily ozone and aged hydrocarbons) that carry over from Friday to Saturday and from Saturday to Sunday help establish initial conditions and boundary conditions that increase ozone concentrations at the surface as the day unfolds.

Hypothetically, pollutants carried over through horizontal or vertical advection have been NO_x limited for many hours because NO_x is depleted more quickly than VOC's during the course of a day. Much of the ozone that is carried over is the product of NO_x limited photochemistry during the late afternoon hours. On weekdays, the formation of ozone aloft during the late afternoon is not registered by surface-based monitoring because fresh NO from the afternoon commute activities depresses the concentrations near these monitors.

Following sunrise, ozone and precursors (radicals?) carried over aloft mix with “today’s” pollutants as mixing heights rise. Similarly, a contaminated air mass may return from horizontal displacement so that the fresh emissions today are mixed into it; that is, fresh emissions are mixed into a NO_x-limited system. On weekdays, the fresh NO emissions overwhelm the carryover component and the system becomes VOC-limited. On Saturday or Sunday, however, the fresh emissions are reduced and the carryover component strongly affects “today’s” photochemistry, making Saturday relatively NO_x-limited and Sunday even more so.

B. Related Evidence

The available data indicate the following in addition to the points noted under the previous hypotheses:

- ratios of ozone to NO_y aloft indicate that carryover aloft may be strongly NO_x-limited
- lidar measurements indicate large reservoirs of ozone from 200 to 1200 meters aloft may be commonplace in the South Coast Air Basin
- lidar measurements indicate that the concentrations of ozone aloft may easily exceed 100 ppb before mixing with the surface layer (1997 data; presumably more ozone in earlier years)
- lidar measurements indicate that fresh ozone is generated aloft following sunrise before the carryover component is mixed with fresh emissions and ozone from the surface layer

4. “Increased Weekend Emissions” Hypothesis

A. Theory

According to this hypothesis, higher weekend ozone levels are caused by increased emissions from certain weekend activities. If this hypothesis is to explain weekend increases in ozone, then the hypothetical emissions increase must occur at most locations in the basin. At least two emission categories – diurnal evaporative emissions and emissions from home maintenance activities – may qualify as ubiquitous. However, routine HC data may not be sufficient at present in space and time to determine whether a weekend increase in HC emissions actually occurs throughout the basin. The routine NO_x data do not indicate a general NO_x decrease rather than an increase at all hours on weekend days compared to weekdays.

Although this hypothesis may not apply generally, ozone at selected sites might reflect local increases in precursors due to weekend increases in some activities.

B. Related Evidence

The available data indicate the following in addition to the points noted under the previous hypotheses:

- several “activities” increase VOC emissions (and NO_x to a lesser extent) on weekends compared to weekdays – these activities include diurnal evaporatives, home maintenance, and recreation, (e.g., motorcycles, boating, barbecues)
- the increase in precursor emissions enhances ozone formation
- these sources have been controlled less vigorously than passenger cars and stationary sources
emission inventories relating to some of these activities are not well developed

5. A Conceptual Framework

Figure 4 presents a conceptual framework that may be useful for organizing data and designing further studies. The inventory data at the left side of the diagram in Figure 4 are taken from a recent Almanac published by the ARB and represent the best information available at that time. Later inventories may alter these data with more reliable values. The air quality data in 1995 for VOC's and NO_x are approximate values based on data from the LA - N. Main and Azusa monitoring sites. In the diagram, the "data" in 1990 and 1985 are computed using the inventory changes and VOC/NO_x ratios are developed from the computed values.

The diagram in Figure 4 may help suggest sampling approaches for filling critical data gaps. For example, VOC and NO_x data for multiple sites representing different subregions of the South Coast Basin are desirable to see whether trends behave according to theoretical expectations. At each site, daily sampling (rather than every nth day) will greatly increase the precision with which days of the week are compared to one another. Furthermore, hourly resolution for both VOC's and NO_x will probably be needed to decide between alternative hypotheses.

Figure 4 also suggests certain questions when evaluating the implications of data with respect to each hypothesis, questions that include the following:

1. How does the hypothesis explain trends by day of week (e.g., 1980 to 1998)? Slower progress on weekends in the last 10 years? Slow progress when NO_x reductions were slight but fast progress when NO_x reductions were substantial (according to inventory numbers)?
2. How does the hypothesis explain differing diurnal profiles in ozone by day of week?
3. How does the hypothesis explain the differences or similarities in day-of-week profiles in different subregions of the Basin?

Figure 1
Nonlinear Ozone Isopleths
(Schematic EKMA Diagram)

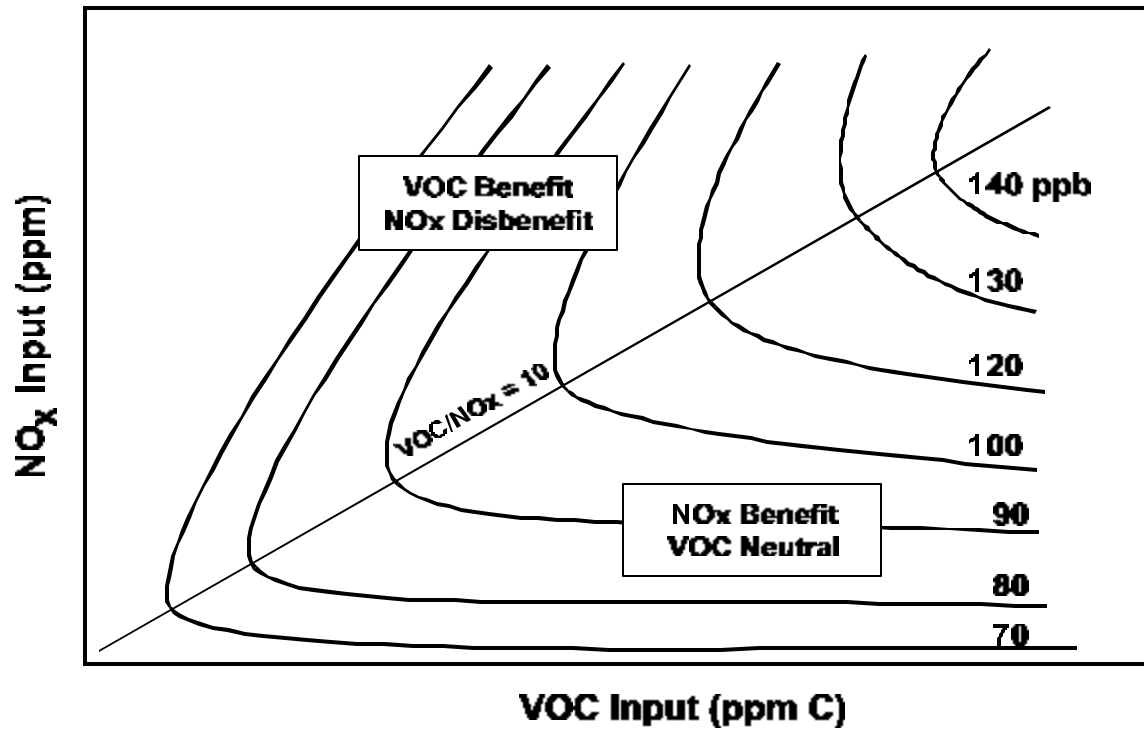


Figure 2. General Character of Laboratory Results for Experiments Concerning Timing of NO_x

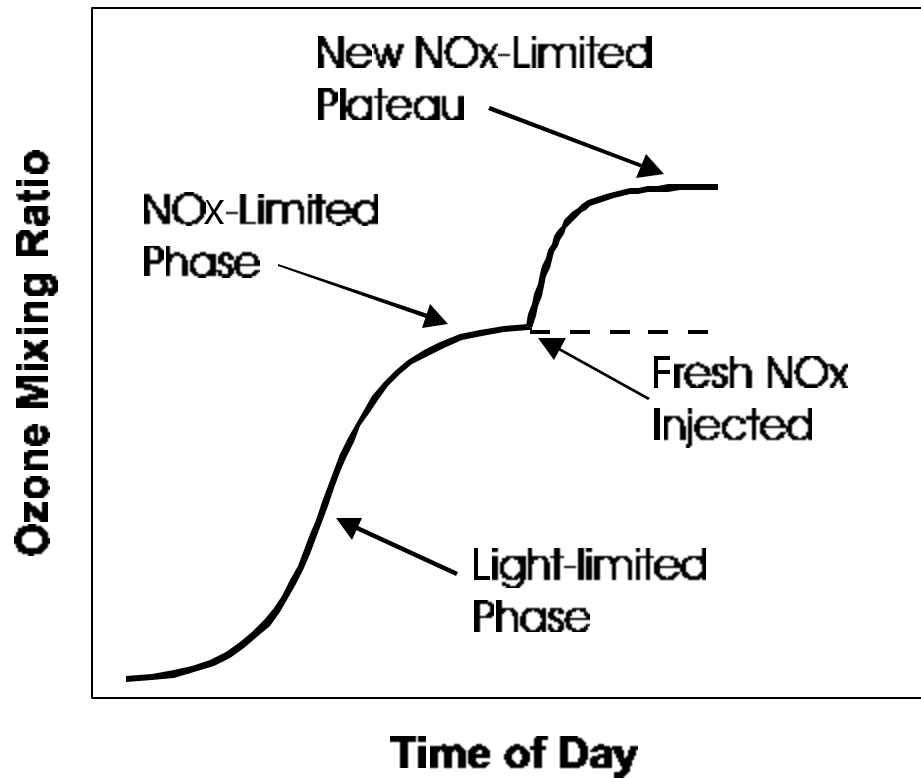


Figure 3. Diurnal Emissions Profiles Before and After Implementing a NO_x Control Strategy
(compared to a Sunday profile)

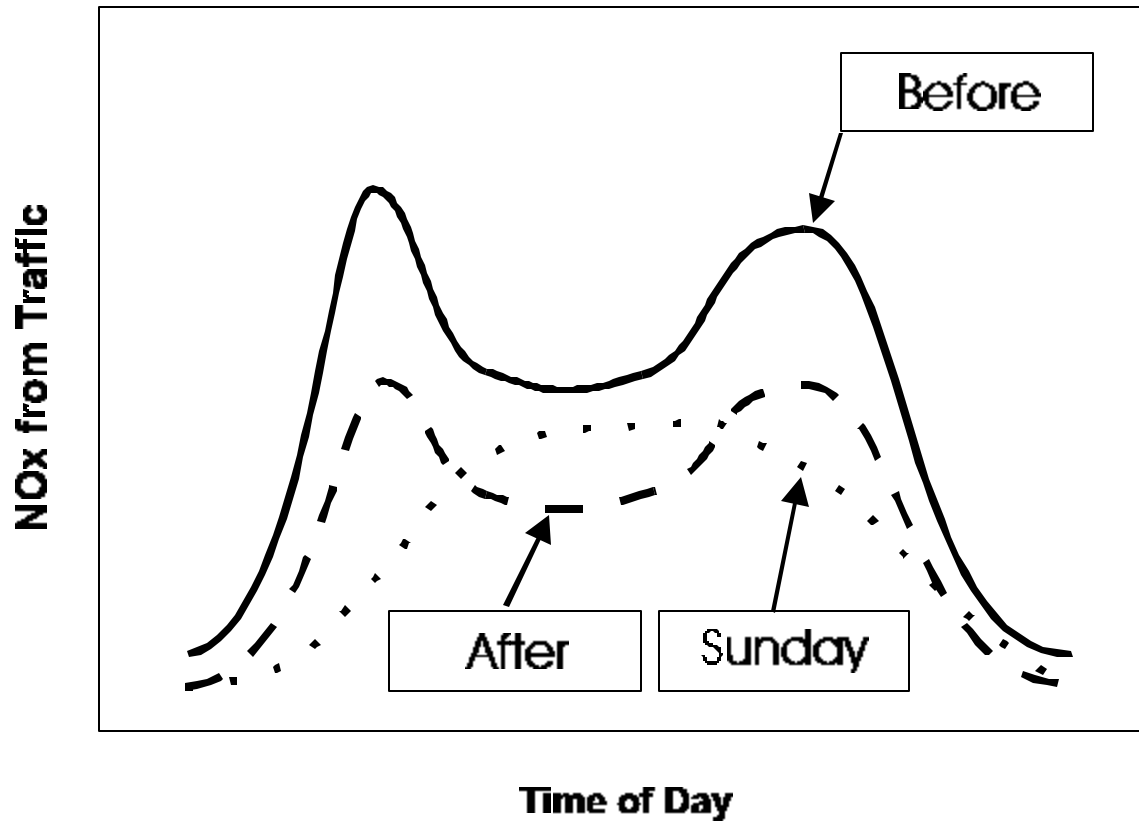
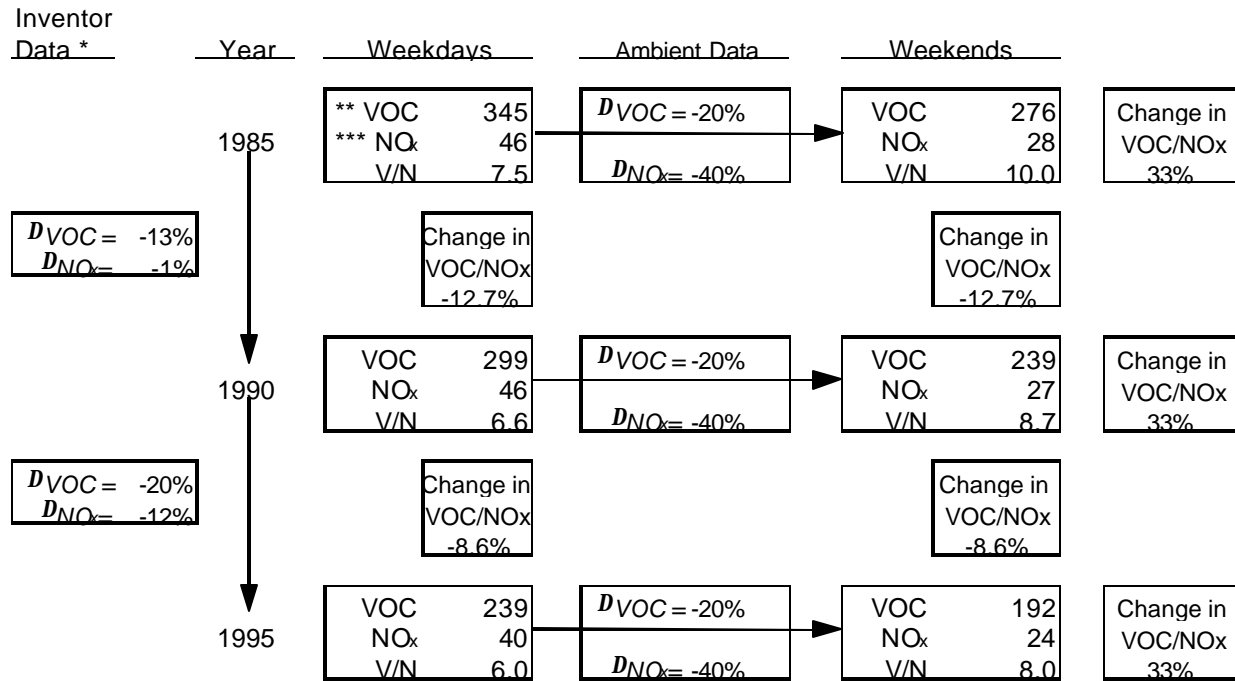


Figure 4. Conceptual Structure of Air Quality and Emissions Inventory for the South Coast Air Basin



* Based on total emissions for the South Coast Air Basin from the 1999 California Almanac of EMISSIONS & AIR QUALITY

** VOC data in ppbC loosely based on data for the L.A. - North Main and Azusa monitoring sites

*** NO_x data in ppb loosely based on data for the L.A. - North Main and Azusa monitoring sites